

THE CHAMELEONIC CARBON SURFACES: ENVIRONMENTAL PROBLEMS AND SOLUTIONS

Ljubisa R. Radovic and Anthony Cugini*

Department of Energy and GeoEnvironmental Engineering
The Pennsylvania State University, University Park, PA 16802

*Department of Energy, Federal Energy Technology Center, Pittsburgh, PA 15206

KEYWORDS: Coal-derived carbons, surface chemistry, coal conversion

1. INTRODUCTION

Among the fossil fuels, the negative environmental impact of coal is typically larger than the impact of either petroleum or natural gas. Considerations of both conventional pollution (acid rain and smog) and global warming (presumably *caused* by CO₂ accumulation in the atmosphere) cast serious doubts on the continued massive use of coal in the 21st century. A simple back-of-the-envelope calculation illustrates the complexity of the problem. While bringing an economic boom to states such as Wyoming, the ongoing market switch from higher-rank, high-sulfur coals (ca. 200-250 lb CO₂/10⁶ BTU) to lower-rank, low-sulfur coals (ca. 300-350 lb CO₂/10⁶ BTU) is making the global warming problem even worse:

$$\frac{72\text{lbC}}{100\text{lbCoal}} \frac{44\text{lbCO}_2}{12\text{lbC}} \frac{1\text{lbCoal}}{8000\text{BTU}} = 330 \frac{\text{lbCO}_2}{10^6 \text{BTU}}$$

$$\frac{82\text{lbC}}{100\text{lbCoal}} \frac{44\text{lbCO}_2}{12\text{lbC}} \frac{1\text{lbCoal}}{14000\text{BTU}} = 215 \frac{\text{lbCO}_2}{10^6 \text{BTU}}$$

While the politics of this issue are daunting -- it remains to be seen how the world will prevent China and India from using coal to fuel their expected economic boom in the 21st century and whether the U.S. will find cost-effective alternatives to coal for electricity generation -- here we shall explore a new concept in carbochemistry (vs. petrochemistry), as an alternative "high-tech" way of continuing to use the world's vast coal resources. We are not advocating the return to carbochemistry of the 19th century, when coal was the source of organic chemicals which gave birth to chemical industry (1). Our main focus is on the fact that the 20th century has ushered in the "age of materials" (2, 3). We argue that a realistic path toward the appealing "natural capitalism" advocated by Amory Lovins for the 21st century (4) naturally includes an increasing role for coal-derived carbons. We are thus proposing a novel concept in coal conversion (see Figure 1): the production of high-value-added carbon materials from *all* of its fractions. The key distinguishing feature of this concept is not that coal will be the raw material for the production of low-cost, high-performance materials such as carbon fibers, even though "Natural Capitalism" advertises these products as a panacea (4). Rather, the novelty of the concept is illustrated in Figure 2. Previous coal conversion concepts were based on tailoring the process toward the manufacture of one or two products; the residue, often a very large fraction of the coal, was then used as a fuel or was discarded. For example, in "mild gasification" (actually coal pyrolysis), which was a popular concept a decade ago, coal-derived liquid fuels are the desired product but the residual char, used as fuel, can represent as much as 70% of the product. There will be no residue in the processes whose concept is being advocated here. As illustrated in Figures 1 and 2 and discussed in more detail below, the processing steps and the intermediate products will be optimized in such a way that each end-product will find a market where its properties will be in most cases superior or at least comparable to existing products. The principal markets (see Figure 1), which are expected to be big in the 21st century *and* are natural outlets for coal-based products, are specialty adsorbents, catalysts, electrodes and electrocatalysts. While the required properties for these materials differ in many important details, they have one important commonality: in addition to optimized physical surface properties (i.e., a specific pore size distribution), superior performance requires careful tailoring of their chemical surface properties (5).

2. COAL-TO-CARBON CONVERSION

This is envisioned as a fractionation process akin to that of coal liquefaction. Taking advantage of the vast industry experience, the products are grouped into preasphaltenes, asphaltenes, oils and (heptane-) insolubles. The conditions we advocate are typical to those often encountered in coal liquefaction, but there is no insistence on maximizing the yield of oils, and thus the expected costs (see Section 7) are not as vulnerable as those of coal liquefaction: <1000 psi N_2 or H_2 , 620-670 K, using a process-derived solvent. The post-fractionation processing steps are discussed below. The feedback loop in Figure 1 illustrates the key issue: do the process conditions used and the selection of a particular coal result in an optimum yield and quality of the intermediate and final products? The affirmative answer to this question relies on our ability to practice molecular engineering by heat treatment of the fractions and chemical modification of the intermediate products (see Figure 1). This in turn gives us the ability to control crystallite alignment and property anisotropy development in the final products. The optimum yield issue is briefly addressed in Section 7. The quality issue is outlined in Sections 3-6.

3. SPECIALTY ADSORBENTS FROM COAL

Coal-derived activated carbons for air and water cleanup have become commodity products, at a typical cost of \$1/lb. There is now some irony in future developments: the research required for better products is hampered by this commodity status and by global-economy competition. And yet the increasingly stringent legislation on clean air and clean water do require vast improvements in the performance of activated carbons. The way out of the impasse is the development of specialty adsorbents. In recent years it has become obvious that in the use of carbons for water treatment in particular (e.g., removal of phenols), but also for removal of gases and vapors where at least interfering moisture effects are present (e.g., SO_x and NO_x removal from air, gas storage), the chemistry of the adsorbent surface is often the dominant factor (6, 7). Both the nature of the coal and the conditions of coal and carbon processing are highly adaptable to the production of a desired surface chemistry in the final product. Thus, for example, all the intermediate products except oils (see Figure 2) are suitable precursors for specialty carbon adsorbents. Their porosity and surface area development ("activation") may not require a preoxidation step (as is the case in conventional preparation of activated carbons from bituminous coals) and their chemical modification can make the surface either highly acidic (and hydrophilic) or highly basic (and hydrophobic).

4. CATALYSTS FROM COAL

Carbon materials are known to have unique properties in catalysis, both as supports and as catalysts in their own right (8, 9). Even though this is a relatively mature market, almost as mature as that of activated carbons, the opportunities for tailoring chemical surface properties for optimum performance are practically virgin territory. The issues here are similar to those outlined in Section 3: catalytic activity depends at least on the surface area of the catalyst, which in turn can be tailored by optimizing the surface chemistry and physics of the support. But it also depends on the electronic structure of the carbon, either directly (electron transfer in the catalyzed reaction of interest) or as a consequence of the often desirable catalyst/support interaction. Two examples will suffice to illustrate the tremendous opportunities here for coal-derived carbons. In the pharmaceutical and fine-chemicals industries, carbon-supported noble metal catalysts are widely used and yet poorly understood; in the processing scheme shown in Figure 2, each one of the products will have a unique combination of bulk (e.g., electronic) and surface properties, depending on the degree of carbon crystallite growth and alignment, which is controlled in turn by selecting the starting coal and the processing conditions. Even carbons produced by vapor cracking (e.g., P3 in Figure 2), used without surface modification, offer unique catalytic properties; a good example is the family of oxidative dehydrogenation reactions (e.g., of ethylbenzene), where carbon is now known to play a key role (8, 10) even though the (nominal) catalyst is alumina-based.

5. ELECTRODES FROM COAL

The necessary combination of optimized bulk and surface properties, which is generated naturally in the coal-derived carbons proposed here, is a *sine qua non* condition in high-performance electrodes. Here we have in mind not so much the conventional markets (e.g., steel and aluminum manufacturing); we see untapped opportunities primarily in the booming and yet very deficient market of rechargeable batteries (11) and supercapacitors. Because this is such an interdisciplinary application, with required inputs from coal and materials scientists, as well as from carbon scientists and electrochemists, successful development of (ash-free) superior products will be possible only through implementation of the *entire* spectrum of carbon characterization tools shown in Figure 1.

6. ELECTROCATALYSTS FROM COAL

This is the holy grail of energy science and technology. It is also the ultimate challenge for carbon science and technology and it is here that the proposed concept can provide the much needed breakthroughs. Carbon materials are currently used (12, 13) and misused (14) in several types and components of fuel cells. In the "hot" field of polymer-electrolyte-membrane fuel cells, for example, they are not only the electrodes and current collectors but also the diffusion layers and electrocatalyst supports. In each application, the right combination of porous structure, surface chemistry and proton and electron transfer characteristics is required. There is no better opportunity than that afforded by the concept proposed in Figures 1 and 2 to achieve this goal: a cost-effective, high-performance, even perhaps a non-noble-metal carbon-supported electrocatalyst for the reduction of O₂ (as well as hydrogen and/or hydrocarbons).

7. SUMMARY: TECHNO-ECONOMIC OPTIMIZATION

The oversimplified but illustrative equation presented below highlights the key advantage of the proposed concept (see Figure 2).

$$Max \frac{\$}{yr} = \frac{OptlbP1}{yr} \frac{\$}{lbP1} + \frac{OptlbP2}{yr} \frac{\$}{lbP2} + \frac{OptlbP3}{yr} \frac{\$}{lbP3} + \frac{OptlbP4}{yr} \frac{\$}{lbP4}$$

The aromatic character of coal makes it a natural, high-yield raw material for carbon products. And the chameleonic nature of the carbon surface, which can be tailored to produce a variety of either bulk-property-dominated materials (e.g., P3) or surface-active materials (e.g., P1, P2, P4), provides the desired flexibility in exploiting the emerging markets of the 21st century. Both the yields of the products (OptlbP/yr) and their quality or market value (\$/lbP) can thus be optimized and continually fine-tuned for maximum profit (Max\$/yr). This augurs well for an elegant scientific, technological and economic solution to the environmental problems of coal utilization.

ACKNOWLEDGMENTS

This study was made possible by an ORISE grant (Fossil Energy Faculty Research Participation) from the Department of Energy. LRR is grateful to the Fuels and Process Chemistry Division of FETC for their hospitality during his stay in Pittsburgh in August 1999.

REFERENCES

1. F. Aftalion, *A History of the International Chemical Industry* (University of Pennsylvania Press, Philadelphia, PA, 1991).
2. I. Amato, *Stuff: The Materials the World is Made Of* (BasicBooks, New York, 1997).
3. P. Ball, *Made to Measure: New Materials for the 21st Century* (Princeton University Press, Princeton, NJ, 1997).
4. P. Hawken, A. Lovins, L. H. Lovins, *Natural Capitalism: Creating the Next Industrial Revolution* (Little, Brown and Company, Boston, 1999).
5. C. A. Leon y Leon, L. R. Radovic, in *Chemistry and Physics of Carbon*, P. A. Throver, Ed. (Marcel Dekker, Inc., New York, 1994), Vol. 24, pp. 213-310.
6. L. R. Radovic, J. I. Ume, A. W. Scaroni, in *Fundamentals of Adsorption* M. D. LeVan, Ed. (Elsevier, Amsterdam, 1996) pp. 749-756.

7. L. R. Radovic, in *Surfaces of Nanoparticles and Porous Materials* J. A. Schwarz, C. I. Contescu, Eds. (Marcel Dekker, New York, 1999) pp. 529-565.
8. L. R. Radovic, F. Rodriguez-Reinoso, in *Chemistry and Physics of Carbon*, Vol. 25, P. A. Thrower, Ed. (Marcel Dekker, New York, 1997) pp. 243-358.
9. L. R. Radovic, C. Sudhakar, in *Introduction to Carbon Technologies*, H. Marsh, E. A. Heintz, F. Rodriguez-Reinoso, Eds. (University of Alicante Press, Alicante, Spain, 1997).
10. A. E. Lisovskii, C. Aharoni, *Catal. Rev. Sci. Eng.* **36**, 25-74 (1994).
11. S. Flandrois, B. Simon, *Carbon* **37**, 165-180 (1999).
12. K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties* (Wiley-Interscience, New York, 1988).
13. H. Wang, R. Côté, G. Faubert, D. Guay, J. P. Dodelet, *J. Phys. Chem. B* **103**, 2042-2049 (1999).
14. L. R. Radovic, *in preparation* (2000).

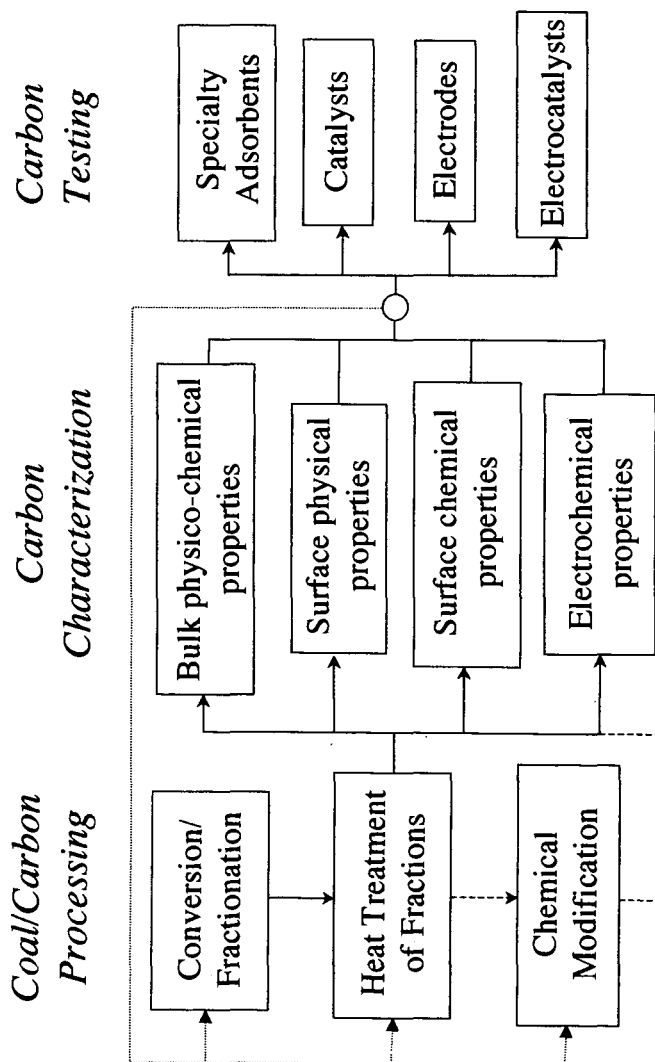


Figure 1
R&D flow diagram of an environmentally benign, technologically novel and economically flexible process of coal utilization by complete conversion to high-value-added carbon materials.

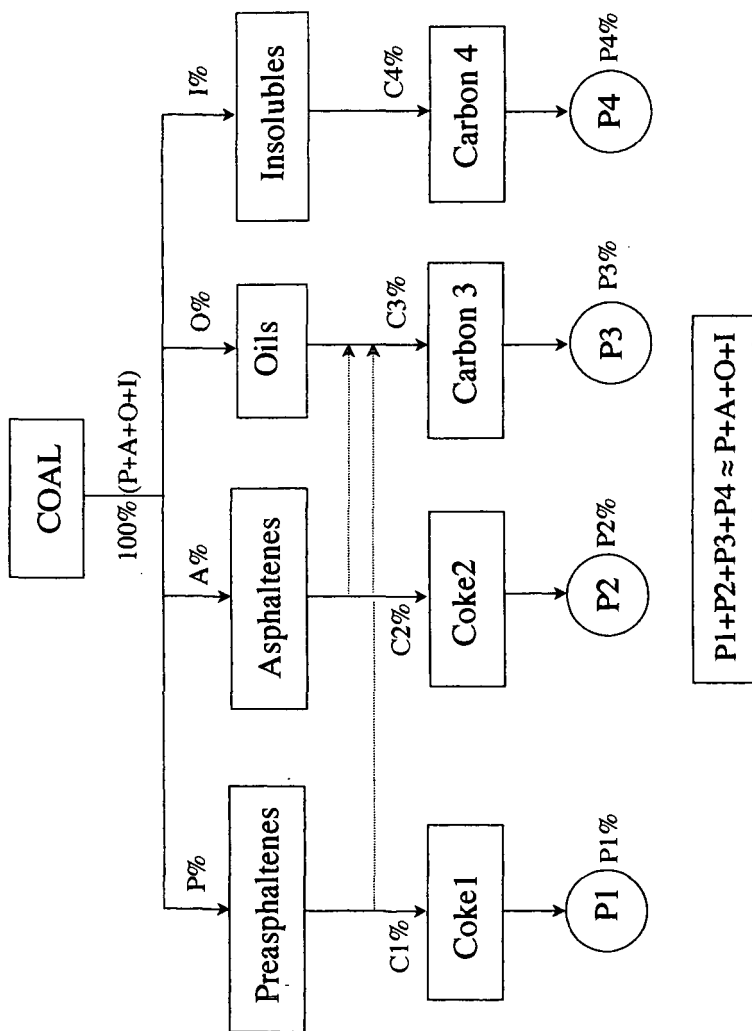


Figure 2. Optimization of the yields of end-products (P1-P4) in the complete conversion of coal to high-value-added carbon materials.